

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PROCESS FOR THE PREPARATION OF AN IRON-CONTAINING
ALUMOSILICATE WITH PENTASIL STRUCTURE

Claims:

1. Process for the preparation of a crystalline iron-containing aluminosilicate with pentasil structure which has iron and aluminium as lattice points, characterised in that the iron-containing aluminosilicate is obtained from a reaction mixture free of organic substances acting as templates and containing compounds of silicon, aluminium, sodium, and iron in addition to hydroxide ions and water in a one-step crystallisation process under hydrothermal conditions at 423 to 473K and addition of nitrate and/or sulfate ions-containing compounds.
2. A process according to claim 1, characterised in that the composition of the reaction partners, expressed in molar ratios of the oxides, is
$$\begin{array}{ll} \text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 & 20 \text{ to } 80 \\ \text{M}_2\text{O}/\text{SiO}_2 & 0.05 \text{ to } 0.5 \\ \text{H}_2\text{O}/\text{SiO}_2 & 5 \text{ to } 150, \text{ and} \\ \text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 & 0.05 \text{ to } 0.7. \end{array}$$
3. A process according to claim 1, characterised in that iron is added in the form of iron nitrate.
4. A process according to claim 1, characterised in that iron is added in the form of iron sulfate.
5. A process according to claim 1, characterised in that use is made of a mixture of iron sulfate and iron nitrate.

6. A process according to claim 1, characterised in that the mixing takes place discontinuously in the vessels provided for the reactions or else continuously in one of the steps introducing the crystallisation.
7. A process according to claim 1, characterised in that the reaction mixture after the mixing at room temperature is left to stand for 1 to 24 hours.

Field of application of the invention

The invention pertains to a process for the preparation of crystalline iron-containing aluminosilicates with a pentasil structure, which can be used advantageously in catalytic processes as catalysts or catalyst components.

Description of the known prior art

Crystalline aluminosilicates because of their specific structural properties are extremely suitable materials for adsorption and catalysis. Especially during the last few years structural types have been developed which make a wide variational range with regard to pore structure and acidity possible. Reaction courses became possible, in part with a higher molecule form selectivity, which cannot be realised with conventional catalysts. Through isomorphic substitution of Al and/or Si in the zeolite lattice by selected elements a further generation of zeolites is developed, the properties of which can be adjusted better to the catalysing reactions. Both the acidity and the pore size can be altered and through the incorporation of heavy metals for instance a hydrogen activation is possible in the lattice.

The zeolites technically used at the time have some drawbacks with regard to their individual acidity. This high individual acidity leads to a lowering of the selectivity with the action time in reactions which do not require strongly acidic centres, such as is for instance the case in the conversion of methanol to olefins or aromatic substances. For such reactions zeolites of the pentasil type prove fit for use.

Compared to the conventional zeolite types A, X, and Y they have in fact a lower number of – but as a result stronger – acidic centres.

Hence the efforts are directed at preparing a zeolite-type material which has no or only a little aluminium and other cations which lend the associated centres only a low individual acidity in lattice positions. Such a material should have a higher selectivity and a longer serviceable life as a catalyst or catalyst carrier.

Such a material is encilite (WHU, HAO, LING: Shiyu Huagong 15 [4] [1986] 219-24, quoted according to C.A.105, 10 115w) with the composition 1.0 ± 0.2 $M_2O:Fe_2O_3:30$ to 200 $SiO_2:z$ H_2O with M for alkali, ammonium or hydrogen and z for 0 to 20. This material is made using organic compounds in the reaction mixture – the so-called template compounds. As templates may be used compounds of the type yR^1xR^2NBr, yR^1xR^2NOH , with R^1 and R^2 being alkyl groups with C_1-C_4 . R^1 and R^2 may be the same or different, x and y are numbers between 1 and 3, with the sum of x and y equalling 4.

As examples are mentioned for instance: triethyl-n-propyl-ammonium bromide, tetrapropyl ammonium bromide, and triethyl-n-butyl-ammonium bromide. As synthesis temperature a range of 100 to 200°C is indicated, as synthesis period 1 to 15 days.

In a further document (DD 0232063) an iron-substituted zeolite material, its preparation and use are claimed. It has the designation FeSO-38. The composition becomes $aM_{2/n}O (Al_xFe_{(1-x)2}O_3:bSiO_2$, wherein M stands for a cation of the valency n, $a = 0$ to 3.5, $b = 3$ to 100, and $x = 0$ to 0.98. The preparation thereof likewise is only possible from reaction mixtures which contain organic template material. As template materials are used: tetraethylammonium compounds such as bromide or hydroxide or triethylamine.

In addition, all organometallic compounds from group N, P, As, Sb, Bi with an alkyl or aryl group (1 to 7 C-atoms), preferably with at least one ethyl group, can be used.

These known preparation processes for iron-containing aluminosilicates with zeolite structure have the crucial drawback that large amounts of expensive organic cations, their starting products or other organic substances suitable as template compounds are required for the synthesis of the iron-containing aluminosilicates. A crucial drawback is that these organic substances, which after the crystal formation are present in the hollow space, have to be removed again to make the hollow space structure and the active centres accessible again to the reactants of the process in question. This can conventionally be done by calcination and in addition to high energy cost requires a waste gas disposal.

A further drawback is created when using template compounds as a result of the necessary and expensive safety techniques and the disposal of the waste products formed in the processing of the synthesis mixture.

Object of the invention

The object of the invention is a process for the preparation of a crystalline aluminosilicate with pentasil structure which has improved adsorptive and catalytic properties and is free of the aforesaid drawbacks of preparation.

Explanation of the nature of the invention

The task of the invention is to find a process for the preparation of a crystalline aluminosilicate with zeolite structure and pentasil structure and altered material properties through isomorphic substitution of aluminium atoms.

According to the invention, a crystalline aluminosilicate with pentasil structure, which has iron and aluminium as lattice points, is obtained from a reaction mixture which is free of organic substances acting as templates and contains compounds of silicon, aluminium, sodium, and iron in addition to hydroxide ions and water in a one-step crystallisation process under hydrothermal conditions at 423 to 473K and addition of nitrate and/or sulfate ions-containing compounds.

It is essential to the invention that the nitrate and/or sulfate ions reach the synthesis mixture through one of the reaction partners. Advantageously, this may be through Fe-, Al- or Na-nitrate or sulfate.

It was surprising that in the presence of nitrate- or sulfate-containing compounds in the reaction mixture the addition of organic substances as template compounds may be omitted, in order to prepare the desired structure with iron atoms in the lattice under hydrothermal conditions.

As sources for the oxides may be used, e.g.:

- for the alkali metal oxides: alkali metal hydroxides and/or alkali metal nitrates
- for aluminium oxide: hydrated or hydratable aluminium oxide, aluminium salts, especially aluminium nitrate and/or sodium aluminate solutions
- for SiO_2 : pyrogens or precipitation silicic acids, silicic acid sols, silica gels, alkali metal silicates, sodium waterglass solutions
- for Fe_2O_3 : iron salts, especially iron nitrates and/or sulfates.

The mixing can take place discontinuously in the vessels provided for the reaction but also continuously in one of the steps introducing the crystallisation.

Typical compositions of the reaction partners, expressed in molar ratios of the oxides, are:

$\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	20 to 80
$\text{M}_2\text{O}/\text{SiO}_2$	0.05 to 0.5
$\text{H}_2\text{O}/\text{SiO}_2$	5 to 150, and
$\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	0.05 to 0.7.

At a reaction temperature of 353 to 493K this mixture is kept under hydrothermal conditions until crystal formation, next the mother liquor is separated, washed, and dried at 383K.

Through 1 to 24-hour ageing of the reaction mixture at room temperature the crystallisation can be accelerated and the homogeneity of the product improved. An acceleration of the crystallisation in addition is also possible through the technique of seeding known to the skilled person.

The thus obtained iron-containing aluminosilicates with pentasil structure have characteristic X-ray diffraction lines, are free of organic constituents, and in the dehydrated state have a composition of 0.8 to 1.5 $\text{M}_2\text{O} : (x \text{Al}_2\text{O}_3 + 1 - x \text{Fe}_2\text{O}_3) : (20 \text{ to } 60) \text{SiO}_2$ with $x = 0.4$ to 0.9 .

For use in e.g. catalysts or adsorption agents the silicates according to the invention can be modified by means of the techniques of ion exchange, impregnation and/or shaping known in the field.

Exemplified embodiments

Example 1

Prepared is a solution of 4.6 g Na-aluminate (c 20 mass% Al_2O_3), 2.13 g NaOH (min. 99%), 179.5 g water, and 1.44 g $\text{Fe}(\text{NO}_3)_3$. To this alkaline solution are added at room temperature under vigorous stirring 86.03 g Na-stabilised silica sol and intensively homogenised. The molar composition of the reaction components is:

$\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	40
$\text{Na}_2\text{O}/\text{SiO}_2$	0.1
$\text{H}_2\text{O}/\text{Na}_2\text{O}$	300
Fe/Al	0.4

The reaction mixture is crystallised at 473K under inherent pressure. After a crystallisation period of 9 hours a product is obtained which has a pentasil structure and the typical X-ray diffraction lines given in Table 1. The water vapour adsorption capacity of the product at $p/p_s = 0.04$ and room temperature is 5.23 mass%.

Table 1

Values of the characteristic X-ray diffraction lines of the iron-containing aluminosilicates according to the invention

Interplanar spacing (nm)	relative intensity
1.11 ± 0.02	st
0.980 ± 0.02	st
0.587 ± 0.01	s
0.557	s
0.548	Ss
0.421 ± 0.01	s
0.386 ± 0.007	sst
0.381 ± 0.007	st
0.372 ± 0.005	m
0.369 ± 0.005	m
0.362	m
0.340	s
0.329 ± 0.003	Ss
0.302	s
0.297	s
0.294	s

Example 2

A solution corresponding to Example 1 is made of 3.06 g Na-aluminate, 2.5 g NaOH, 179.6 ml water, 2.89 g $\text{Fe}(\text{NO}_3)_3$, and 86.03 g Na-stabilised silica sol (30 mass% SiO_2) are added with vigorous stirring at room temperature. The reaction mixture is homogenised. The molar composition of the reaction partners is:

$\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	40
$\text{Na}_2\text{O}/\text{SiO}_2$	0.1
$\text{H}_2\text{O}/\text{Na}_2\text{O}$	300
Fe/Al	0.66

The reaction mixture is brought to crystallisation under inherent pressure at 473K. After 14 h an aluminosilicate with pentasil structure and the typical X-ray diffraction lines corresponding to Table 1 was obtained. The water vapour adsorption capacity at $p/p_s = 0.04$ and room temperature is 4.9 mass%.

Example 3

A reaction mixture corresponding to Example 2 is prepared. To the reaction mixture are added 1.5 g template-free aluminosilicate with pentasil structure, a Si/Al-molar ratio of 15, and the typical X-ray diffraction lines (Table 1). The mixture is again homogenised and crystallised under inherent pressure at 448K. After a crystallisation period of 10 hours a product is obtained which has a pentasil structure and has the typical X-ray diffraction lines given in Table 1. The water vapour adsorption capacity of the product at $p/p_s = 0.04$ and room temperature is 5.14 mass%.

Example 4

A solution is prepared of 4.6 g Na-aluminate (c 20 mass% Al_2O_3), 2.13 g NaOH (min. 99%), 179.5 g water, and 0.74 g FeSO_4 . To this alkaline solution 86.03 g Na-

stabilised silica sol are added at room temperature under vigorous stirring and intensively homogenised. The molar composition of the reaction components is:

$\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	40
$\text{Na}_2\text{O}/\text{SiO}_2$	0.1
$\text{H}_2\text{O}/\text{Na}_2\text{O}$	300
Fe/Al	0.4

The reaction mixture is crystallised under inherent pressure at 493K. After a crystallisation time of 11 hours a product is obtained which has a pentasil structure and has the typical X-ray diffraction lines given in Table 1. The water vapour adsorption capacity of the product at $p/p_s = 0.04$ and room temperature is 4.87 mass%.

Example 5

A solution corresponding to Example 1 is prepared of 3.06 g Na-aluminate, 2.5 g NaOH, 179.6 ml water, and 1.45 g $\text{Fe}(\text{NO}_3)_3$, and 86.03 g Na-stabilised silica sol are added at room temperature under vigorous stirring. The reaction mixture is homogenised. The molar composition of the reaction partners is:

$\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	40
$\text{Na}_2\text{O}/\text{SiO}_2$	0.1
$\text{H}_2\text{O}/\text{Na}_2\text{O}$	300
Fe/Al	0.66

The reaction mixture is crystallised under inherent pressure at 463K. After 16 hours an aluminosilicate with pentasil structure and the typical X-ray diffraction lines corresponding to Table 1 is obtained. The water vapour adsorption capacity of the product at $p/p_s = 0.04$ and room temperature is 4.75 mass%.